

TECHNICAL REPORT No. 7

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New Jersey Ceramic Research Station
Rutgers University

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SPECIFIC HEAT OF VITREOUS SILICA

Abstract

A method is developed for the study of the thermal motions of the atoms in vitreous silica. This enables tentative calculations of specific heat based on various forms of binding between atoms and on vibrations of single atoms independent of their neighbors. First comparisons with experiment are not very satisfactory and methods are developed for the use of larger and larger groups in order to approach more closely to the actual network vibrations.

Introduction

In an earlier paper⁽¹⁾ it was shown that a specific heat curve agreeing reasonably well with the experimentally determined curve could be calculated from a simple model. This model consisted of silicon atoms which could oscillate in three directions with three equal frequencies and oxygen atoms which could oscillate in two transverse directions between pairs of silicon atoms with two equal frequencies and

with a different higher frequency longitudinally between the silicon atoms. The values of the frequencies were not derived from any detailed model of the structure of vitreous silica but were rather chosen to give the best fit with the experimental curve. It seemed worth while to extend this work by trying to derive the curve of specific heat versus temperature for vitreous silica from our knowledge of its structure and some reasonable assumptions as to the nature of the forces between the various atoms making up the structure.

Nature of Interatomic Forces

Considerable doubt exists as to what is a reasonable assumption as to the nature of these forces. On the one extreme there might be considered the purely ionic picture where the forces would be Coulomb attractions or repulsions modified only by repulsions varying with a power of the separation much higher than the second. In this case, in computing the field of force in which each ion moves one must consider the effects arising from a large number of neighbors since the Coulomb forces fall off so slowly with distance.

On the other extreme the forces might be those arising from pure covalent binding. In this case the interatomic interactions would arise only from close neighbors but some doubt would arise as to the exact mathematical form to use to express these interactions. For purely central forces a

Morse⁽²⁾ function might be chosen such as to give the correct heat of formation but the effect of specially directed covalent binding might still be difficult to handle.

In all probability the true picture is somewhere between these two extremes. Pauling,⁽³⁾ on the basis of the electronegativities of silicon and oxygen, describes the binding as 50% ionic. In order to obtain more experimental indication as to the nature of the binding it is justifiable to consider either of the two extremes and use the lack of agreement, if found, as a stepping stone to a more exact description. The present paper considers mostly the ionic model.

Ionic Model of Vitreous Silica

As in a previous paper by Smyth, Londersee and Lorey,⁽⁴⁾ each silicon ion is considered to be contained in the field arising from four oxygens tetrahedrally arranged around the silicon, four silicons at twice this Si-O distance and lying along the extension of the Si-O lines and twelve oxygens at a slightly greater distance. Only one half of the effect of these twelve oxygens is considered so that the charge on those ions affecting each silicon ion is -4 and the remaining structure outside these is considered as neutral and, because of the increasing randomness of the glass structure at these separations giving effects, which, averaged over the whole structure will be effectively zero.

Similarly each oxygen ion is contained in the field of:

- (1) Two Si ions diametrically opposed to each other.
- (2) Six oxygens. (The remaining nearest neighbors of the above two silicon ions).
- (3) One fourth of the six silicon ions at the second closest Si-O distance.

These surroundings exactly balance the charge of -2 on each oxygen ion. The effect of the remainder of the structure is neglected, being neutral.

The question of the validity of neglecting these neutral surroundings is one which deserves a more rigorous treatment beyond the scope of this paper. In crystals, because of the regularity of structure it cannot be neglected but must be exactly considered, as in the methods of Ewald⁽⁵⁾ and others. The assumption is made here, however, that the lack of a regularly repeating structure beyond the neighbors considered justifies our neglect of any contribution to the electrostatic field from this source. Any conclusions reached must therefore be subject to critical examination from the standpoint of this particular assumption.

Calculation of Frequencies

As a first approach to the problem of studying the vibrations of the atoms it might be considered, as in the Einstein theory of specific heats of crystals, that each atom

vibrates in a manner independent of the motions of its neighbors and in the field which would arise from all of its neighbors being in their equilibrium positions. Later there shall be taken up the problem of allowing also for the effects of the vibrations of each atom on its neighbors.

The restoring force acting on any atom when it is displaced a distance u in any direction from its equilibrium position is the same in direction and magnitude as if it had been at rest and all of the other atoms had been moved a distance u in the opposite direction. The first problem is therefore to compute the force acting on an ion at the origin if an ion of known charge at some location (a, b, c) is displaced to a new nearby position $(a+u, b+v, c+w)$. This must take into account both the Coulomb forces and also the higher power repulsions which are important for very near neighbors.

As far as the Coulomb forces are concerned this is equivalent to finding the electric field at the origin arising from a dipole placed at (a, b, c) whose axis is parallel to the displacement (u, v, w) and whose magnitude is the charge on the ion at (a, b, c) multiplied by the linear displacement. This is a well known expression worked out in any text book on electromagnetic theory.⁽⁶⁾ Putting it in the form convenient to the problem in hand the expression may be written:

$$F_x = - \frac{e_1 e_2}{r^3} \left\{ u - 3 \frac{a^2 u + abv + acw}{r^2} \right\} \quad (1A)$$

$$F_y = - \frac{e_1 e_2}{r^3} \left\{ v - 3 \frac{abu + b^2 v + bcw}{r^2} \right\} \quad (1B)$$

$$F_z = - \frac{e_1 e_2}{r^3} \left\{ w - 3 \frac{acu + bcv + c^2 w}{r^2} \right\} \quad (1C)$$

where F_x , F_y and F_z are respectively the x, y and z components of the force on an ion of charge e_1 at the origin due to displacement (u, v, w) on an ion of charge e_2 located at (a, b, c) , and r is the distance from the origin to the point (a, b, c) so that

$$r^2 = a^2 + b^2 + c^2 \quad (2)$$

It might be mentioned that these relations hold rigidly only when the displacements are small compared with the interionic distances involved.

The forces arising from the higher power repulsions can be expressed in very much the same form. If the ion at the origin and the ion at (a, b, c) repel each other with a force of magnitude

$$\frac{A}{r^n} \quad (3)$$

when separated a distance r from each other then the components of the force on the ion at the origin when the ion at (a, b, c) is displaced an amount (u, v, w) are:

$$F_x = -\frac{A}{r^{n+1}} \left\{ u - (n+1) \frac{a^2 u + abv + acw}{r^2} \right\} \quad (4A)$$

$$F_y = -\frac{A}{r^{n+1}} \left\{ v - (n+1) \frac{ab u + b^2 v + bcw}{r^2} \right\} \quad (4B)$$

$$F_z = -\frac{A}{r^{n+1}} \left\{ w - (n+1) \frac{ac u + bc v + c^2 w}{r^2} \right\} \quad (4C)$$

Here the approximation is not quite so good and the neglecting of higher powers of u, v and w than the first becomes less and less justified as n increases.

The model to be used in calculating the natural frequencies of each ion can now be set up and the mathematical expressions worked out for these frequencies.

Ionic Model

The interactions considered in this treatment will be:

(1) Coulomb interactions between each ion and those neighbors previously discussed.

(2) Repulsions of the form $\frac{A}{r^n}$ between each silicon ion and its closest oxygen neighbors.

(3) Repulsions of the form $\frac{B}{r^n}$ between each oxygen and its closest oxygen neighbors.

Repulsions, other than electrostatic repulsions will not be considered between silicon ions and their nearest silicon neighbors or between any pairs of ions with greater separations.

In order to compute the frequencies of a silicon ion the following arrangement is considered. The silicon ion placed at the origin. Its neighbors are located as follows:

(1) Four oxygen ions at (s, s, s) , $(s, -s, -s)$, $(-s, s, -s)$ and $(-s, -s, s)$. These are tetrahedrally arranged about the silicon ion at a distance r_1 such that

$$r_1^2 = 3s^2$$

(2) Four silicon ions at $(2s, 2s, 2s)$, $(2s, -2s, -2s)$, $(-2s, 2s, -2s)$ and $(-2s, -2s, 2s)$.

These are at a distance r_2 such that $r_2 = 2r_1$

(3) Twelve oxygen ions at
 $(3s, 3s, s)$ $(3s, s, 3s)$ $(s, 3s, 3s)$
 $(-3s, -3s, s)$ $(-3s, -s, 3s)$ $(-s, -3s, 3s)$
 $(3s, -3s, -s)$ $(3s, -s, -3s)$ $(s, -3s, -3s)$
 $(-3s, 3s, -s)$ $(-3s, s, -3s)$ $(-s, 3s, -3s)$

The total effect of these twelve will be computed and then

divided by two so that the neighbors altogether will just exactly balance the charge of the silicon ion at the origin, while we at the same time avoid the necessity of making invidious distinctions between these twelve oxygen ions. Each group of three of these oxygens, together with one of the oxygens of group (1) tetrahedrally surround one of the silicons of group (2). Each of these oxygens is a distance r_3 from the origin where

$$r_3 = \frac{\sqrt{19}}{3} r_1 \quad (5)$$

All of these neighbors (1), (2) and (3) will be displaced an amount (u, v, w) and the resultant force on the silicon ion at the origin computed.

Using equations 1A, 1B and 1C it can be easily shown that if all of the oxygens at distance r_1 from the origin are given the same small displacement (u, v, w) the electrostatic forces alone give a zero resulting force on the silicon ion at the origin. Also if all of the silicons at distance r_2 or all of the oxygens at distance r_3 are displaced by the same displacement (u, v, w) the resulting force on the silicon ion at the origin is zero. Hence, if all of these neighbors are held at rest and the silicon ion is given a small displacement there is no restoring force arising from electrostatic attractions or repulsions. All of the restoring force on the silicon ion arises from the higher power repulsive forces of its neighboring oxygens (if we can neglect the effect of the high power repulsions of more distant ions).

Using equations 4A, 4B and 4C it can then be shown that if the four oxygens in group (1) are given each a displacement of (u, v, w) then the resulting force components on a silicon at the origin will be

$$F_x = \frac{4}{3}(n-2) \frac{A}{r_1^3} u \quad (6A)$$

$$F_y = \frac{4}{3}(n-2) \frac{A}{r_1^3} v \quad (6B)$$

$$F_z = \frac{4}{3}(n-2) \frac{A}{r_1^3} w \quad (6C)$$

from which it can immediately be deduced that if a silicon ion is given a displacement u in any direction it experiences a restoring force

$$\frac{4}{3}(n-2) \frac{A}{r_1^3} u$$

in the exactly opposite direction. The field in which it moves is quite spherically symmetrical for small displacements.

Forces on Oxygen Ions

In the case of oxygen ions more attention has to be paid to the direction of displacement. It is obvious that there is likely to be a difference in the restoring force depending on whether the displacement is along the line of the two neighboring silicon ions or transverse to it. It will be shown that if three mutually perpendicular directions are chosen such that one of them lies along the silicon-silicon direction then displacements and vibrations in any one of these directions are independent of what is happening in the other two. This does not hold for three mutually perpendicular directions not so chosen. The model will be set up as follows:

The oxygen ion in question will be located at the origin. Its neighbors will be:

- (1) Two silicons at (s, s, s) and $(-s, -s, -s)$
- (2) Six oxygens at $(2s, 2s, 0)$ $(2s, 0, 2s)$ $(0, 2s, 2s)$ $(-2s, -2s, 0)$ $(-2s, 0, -2s)$ $(0, -2s, -2s)$. These are at a distance r_1 where $r_1^2 = 8s^2$ or $r_1 = \sqrt{\frac{8}{3}} r$
- (3) Six silicons at $(3s, 3s, -s)$ $(3s, -s, 3s)$ $(-s, 3s, 3s)$ $(-3s, -3s, s)$ $(-3s, s, -3s)$ $(s, -3s, -3s)$. Of this last group

we divide the total effect by four for the same reasons discussed previously.

In order to study longitudinal vibrations (i.e. along the silicon-silicon line) a displacement of (u, u, u) will be imposed in place of the general displacement (u, v, w) used for the silicon ion.

A displacement of (u, u, u) imposed on the two silicon ions in group (1) gives rise (using equations 1A, 1B and 1C) to an electrostatic force on the oxygen at the origin whose components are:

$$F_x = - \frac{32 e^2 u}{r_1^3} \quad (7A)$$

$$F_y = - \frac{32 e^2 u}{r_1^3} \quad (7B)$$

$$F_z = - \frac{32 e^2 u}{r_1^3} \quad (7C)$$

Therefore a displacement of u along the silicon-silicon line of the oxygen ion at the origin brings to bear on it an electrostatic force of

$$+ \frac{32 e^2 u}{r_1^3} \quad (8)$$

meaning that as far as the electrostatic attractions of the two silicons alone are concerned the oxygen would be in unstable equilibrium.

Using equations (4A, 4B, and 4C) the force on the oxygen at the origin arising from higher power repulsions of the two silicons is

$$- \frac{2An}{r^{n+1}} u \quad (9)$$

for a displacement u of this oxygen along the silicon-silicon line. This leads to stable equilibrium.

A displacement u of the oxygen ion at the origin along the silicon-silicon line will, because of electrostatic forces from the six oxygens in group (2) give rise to a force on the oxygen ion of

$$- \frac{24 e^2 u}{r_4^3} \quad (10)$$

The repulsive forces of these six oxygens give a force on the oxygen moved longitudinally a distance u of

$$- \frac{2B}{r_4^{n+1}} (2n-1) u \quad (11)$$

The six silicons in group (3) will cause a force (purely electrostatic) on the oxygen when moved a distance u along the silicon-silicon line of

$$\frac{288 e^2 u}{14 r_2^2} \quad (12)$$

Again the two groups of attracting ions pulling against each other tend to produce unstable equilibrium. Of this quantity only one quarter is considered for reasons already discussed leaving

$$\frac{12}{19} \frac{e^2}{r_3^3} u \quad (13)$$

Using the relations that

$$\begin{aligned} r_1^2 &= 3 s^2 \\ r_2^2 &= 12 s^2 \\ r_3^2 &= 19 s^2 \\ r_4^2 &= 8 s^2 \end{aligned}$$

the complete effect may be summed up. The resultant force on an oxygen ion displaced a distance u along the silicon-silicon line is

$$\frac{32e^2u}{r_1^3} - \frac{24e^2u}{r_2^3} + \frac{72}{19} \frac{e^2u}{r_3^3} - \frac{2An}{r_1^{n+1}}u - \frac{2B}{r_1^{n+1}(2n-1)}u \quad (14)$$

or arranging it all in terms of r_1 , the nearest silicon oxygen distance, and going through the various numerical calculations, the final result is

$$\left[26.73 \frac{e^2}{r_1^3} - \frac{2An}{r_1^{n+1}} - \left(\frac{5}{8} \right)^{\frac{n+1}{2}} \frac{2B}{r_1^{n+1}(2n-1)} \right] u \quad (15)$$

It so happens that the second and third term together are numerically greater than the first resulting in stable equilibrium. The restoring force increases as γ_1 is decreased.

Transverse Oxygen Vibrations

To study vibrations of the oxygen ion in a direction perpendicular to the silicon-silicon line each other ion is given a displacement perpendicular to this line. The direction cosines of the silicon-silicon line are $(\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}})$. A direction with direction cosines (l, m, n) will be perpendicular to this if $l + m + n = 0$. If therefore each ion is given a displacement $\{u, v, -(u+v)\}$ where u and v are arbitrary this displacement will always be perpendicular to the longitudinal direction and proper choice of the ratio of u to v will cover all possible such transverse directions. It will be shown that in each case the restoring force will make an angle of 0 or 180° with the displacement. This holds only for displacements parallel to or perpendicular to the longitudinal direction and would not hold for any direction in between (except for the special case whether the restoring forces in the longitudinal and transverse directions are the same).

First the two silicons at (s, s, s) and $(-s, -s, -s)$ are given a displacement $\{u, v, -(u+v)\}$. From equations 4A, 4B and 4C, the components of the force on the oxygen ion at $(0, 0, 0)$ are

$$F_x = \frac{16e^2}{r_1^3} u \quad (16A)$$

$$F_y = \frac{16e^2}{r_1^3} v \quad (16B)$$

$$F_z = -\frac{16e^2}{r_1^3} (u+v). \quad (16C)$$

Therefore if the oxygen ion is given a displacement u in a transverse direction there is exerted on it a force

$$-\frac{16e^2}{r_1^3} u$$

which means a positive restoring force back along this same direction.

The repulsions of these two silicons give rise to a force

$$\frac{2A}{r_1^{n+1}} u \quad (17)$$

if the oxygen is given a displacement u in a transverse direction.

Similarly the six oxygens of group (2) by electrostatic action give a force of

$$\frac{12e^2}{r_4^3} u. \quad (18)$$

on an oxygen ion at the origin moved transversely a distance u . The non-Coulomb repulsions of these oxygens give a force of

$$\frac{B}{r_+^{n+1}} (5-n) \cdot u \quad (19)$$

Taking one quarter of the effect of the electrostatic effect of the six silicons at r_3 there is obtained for the force acting on an oxygen at the origin displaced transversely a distance u

$$- \frac{36 e^2}{r_3^3} u \quad (20)$$

The complete transverse effect may then be summed up to give

$$- \frac{16 e^2}{r_1^3} u + \frac{12 e^2}{r_+^3} u - \frac{36 e^2}{14 r_3^3} u + \frac{2A}{r_1^{n+1}} u + \frac{B}{r_+^{n+1}} (5-n) \cdot u \quad (21)$$

Putting this in terms of r_1 only there is obtained

$$-13.36 \frac{e^2}{r_1^3} + \frac{2A}{r_1^{n+1}} u + \left(\frac{3}{8}\right)^{\frac{n+1}{2}} \frac{B}{r_1^{n+1}} (5-n) \cdot u$$

Stability depends on the first term being numerically greater than the sum of the other two. The restoring force here decreases as r_1 decreases.

Choice of Constants

There remains the problem of selecting the most probable values for A, B and n . According to Fowler⁽⁷⁾ two neon like ions might be expected to repel each other with a force varying as the inverse eleventh power of the separation and n is therefore taken as eleven. Furthermore there is listed also in Fowler a value for B giving the magnitude of the interaction between two oxygen ions. This value is if r is measured in centimeters and the force in dynes.

$$B = 17.6 \times 10^{-88} \quad (23)$$

A must then be chosen so that the energy of the network is a minimum for the known value of the silicon-oxygen separation in vitreous silica.

Energy of Network

Limiting attention to interactions between each ion and those neighbors previously considered it may be easily shown³ that the electrostatic contribution to the energy of the network is

$$-\frac{32e^2}{r_1} + \frac{32e^2}{r_2} - \frac{36e^2}{r_3} + \frac{24e^2}{r_4} \quad (24)$$

which is a quantity becoming increasingly negative as r_1 , (along with r_2 , r_3 and r_4 in the same ratio) is decreased. This reduces to

$$-15.61 \frac{e^2}{r_1}$$

This negative energy is offset by the positive energy arising from the repulsions between ions as they come close together. For the structure considered this is

$$\frac{4A}{(n-1)r_1^{n-1}} + \frac{6B}{(n-1)r_4^{n-1}} \quad (26)$$

The total energy is therefore

$$-15.61 \frac{e^2}{r_1} + \frac{4A}{(n-1)r_1^{n-1}} + \frac{6B}{(n-1)(\frac{3}{8})^{\frac{n-1}{2}} r_1^{n-1}} \quad (27)$$

The equilibrium distance r_1^0 will be such that this energy is a minimum or that its derivative with respect to r_1 will be zero.

Hence

$$15.61 \frac{e^2}{r_1^2} - \frac{4A}{r_1^n} - \left(\frac{3}{8}\right)^{\frac{n-1}{2}} \frac{6B}{r_1^n} = 0 \quad (28)$$

from which

$$A = 3.402 C^2 r_1^{n-2} - \left(\frac{3}{8}\right)^{\frac{n-1}{2}} 1.5 B \quad (29)$$

Using

$$C = 4.77 \times 10^{-10} \text{ e.s.u.}$$

$$r_1 = 1.62 \times 10^{-8} \text{ cm}$$

$$B = 17.6 \times 10^{-88}$$

$$n = 11$$

$$3.90200 C^2 r_1^{n-2} = .682 \times 10^{-88}$$

$$\frac{1.5 B}{\left(\frac{3}{8}\right)^{\frac{n-1}{2}}} = .196 \times 10^{-88}$$

Hence

$$A = .486 \times 10^{-88} \quad (30)$$

Calculation of Frequencies

Equations (6), (15) and (22) may now be used to compute in actual numerical values the restoring forces on the oxygen and silicon ions, and hence calculate the natural frequencies of oscillation of each of the three different modes of vibration.

For a silicon ion displaced in any direction the restoring force is

$$178.50 \times 10^4 \text{ dynes per cm.} \quad (31)$$

For a longitudinal displacement of an oxygen ion the restoring force is

$$247.13 \times 10^4 \text{ dynes per cm.} \quad (32)$$

For a transverse displacement of an oxygen ion it is

$$50.75 \times 10^4 \text{ dynes per cm.} \quad (33)$$

If the restoring force per unit displacement of a mass m is k then the frequency of oscillation is

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad (34)$$

Using the known masses of the silicon and oxygen ions, the frequency is easily computed. The relation connecting frequency with the characteristic temperature (τ) to be used

in the Einstein specific heat functions is

$$\Theta = \frac{h\nu}{k} \quad (35)$$

where h is Planck's constant and k is Boltzmann's constant.

Table I lists these numbers for the three modes of vibration.

Table I

| <u>Ion</u> | <u>Direction of Vibration</u> | <u>Characteristic Temperature</u> |
|------------|-------------------------------|-----------------------------------|
| Silicon | All | Θ_s 1495° |
| Oxygen | Longitudinal | Θ_L 2328° |
| Oxygen | Transverse | Θ_t 1054° |

The specific heat can be calculated from these characteristic temperatures using the relation

$$C_m = \frac{R}{M} \left\{ 3 \bar{E}\left(\frac{\Theta_s}{T}\right) + 2 \bar{E}\left(\frac{\Theta_L}{T}\right) + 4 \bar{E}\left(\frac{\Theta_t}{T}\right) \right\} \quad (36)$$

where $\bar{E}(x)$ is the usual Einstein function

$$\bar{E}(x) = \frac{x^2 e^x}{(e^x - 1)^2} \quad (37)$$

R is the gas constant and M is the molecular weight of silica. The specific heat computed in this way is shown plotted in fig. 1⁸ along with the experimental values. The agreement is not good, and the theory must be examined to find where it should be modified to give better agreement with experiment. By comparison with values of the characteristic temperatures which have to be assumed to get reasonably good agreement the characteristic temperatures used here are all too high which means the frequencies also are too high.

Before raising the question of the validity of the completely ionic model, it is expedient to examine how the Einstein treatment of the specific heat can be modified to permit an approach toward the Debye method while retaining at the same time the connection between the calculations and the atomic model. The characteristic frequencies have been calculated on the assumption that each ion vibrates in a manner independent of the vibrations of its neighbors which is obviously not the case. If an ion is displaced from its equilibrium the effect at each other ion is as if, to a first approximation, there were added, at the location of the displaced ion a dipole of moment equal to the charge on the ion multiplied by its displacement. Each vibrating ion therefore creates a harmonically varying field at the location of each other ion of a magnitude and direction which depends on the

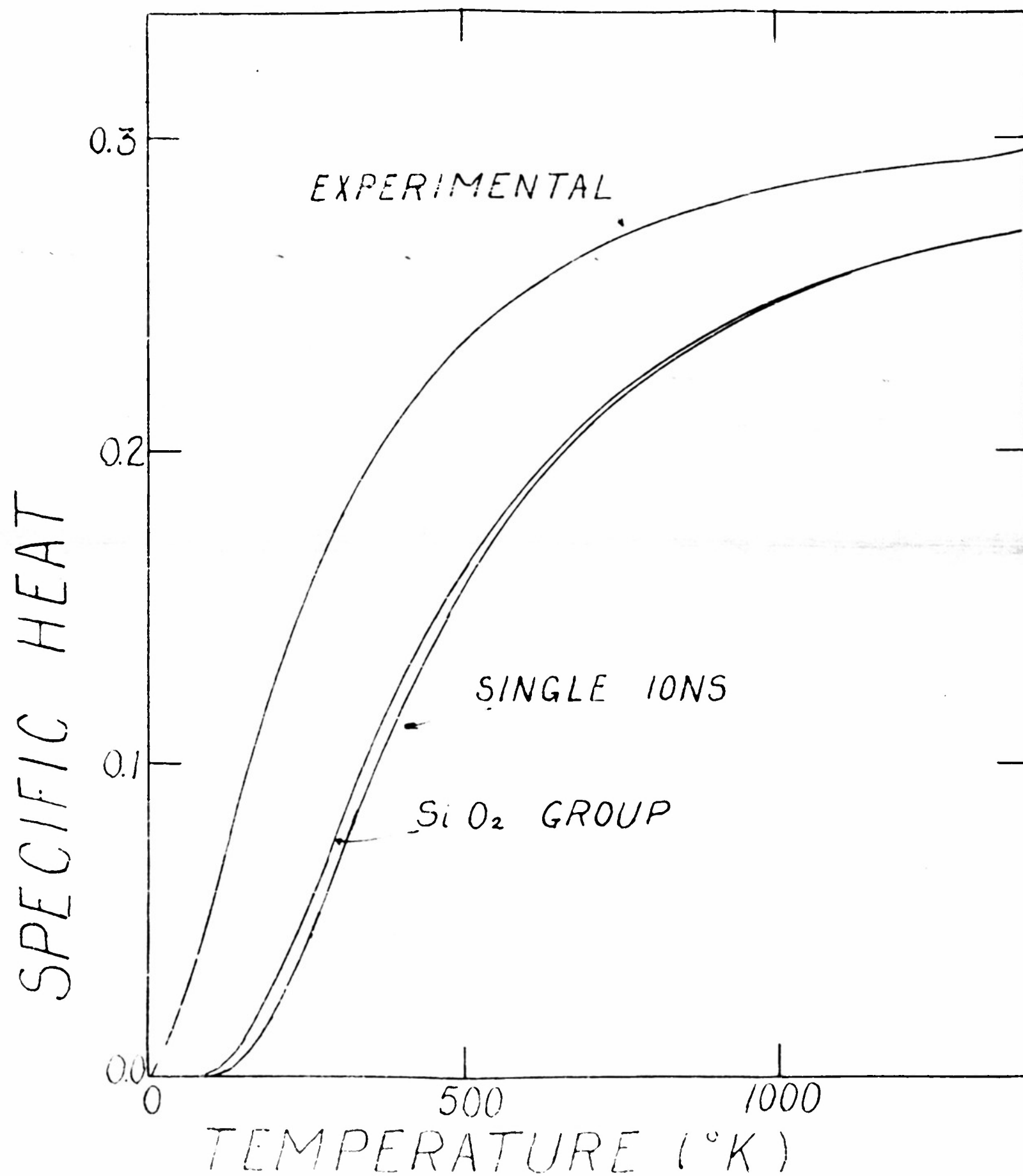


FIG 1

geometry of each pair of ions. In very much the same way as equations 1A, 1B and 1C were derived it can be shown that if an ion of charge e_2 at the point (a, b, c) is displaced a distance u in a direction whose direction cosines are (l_2, m_2, n_2) then there is exerted on an ion of charge e_1 at the origin a force whose component in the direction (l_1, m_1, n_1) is:

$$-\frac{e_1 e_2}{r^3} \left\{ (l_1 l_2 + m_1 m_2 + n_1 n_2) u - \frac{3u}{r^2} (l_1 a + m_1 b + n_1 c) (l_2 a + m_2 b + n_2 c) \right\} \quad (38)$$

where $r^2 = a^2 + b^2 + c^2$

The effect of the repulsion terms can be considered in much the same way and the result is that if two ions distance r from each other repel each other with a force

$$\frac{A}{r^2} \quad (39)$$

then the component of force along the (l_1, m_1, n_1) direction exerted on the ion at the origin by a displacement u of the ion at (a, b, c) in a direction (l_2, m_2, n_2) is

$$-\frac{A}{r^{n+1}} \left\{ (l_1 l_2 + m_1 m_2 + n_1 n_2) u - \frac{(n+1)u}{r^2} (l_1 a + m_1 b + n_1 c) (l_2 a + m_2 b + n_2 c) \right\} \quad (40)$$

Instead then of handling one ion independent of the motions of its neighbors one may then select a group such as, for instance, a single SiO_2 group or two SiO_2 groups tied together or a group of say, five SiO_2 's arranged in a compact unit and study the vibrations of one of these group as a whole instead of merely each isolated ion. In each case the ions outside the group under study will be considered as being at rest. The frequencies will then be the frequencies of the independent modes of vibration of the group as a whole and in this way one might expect to find some modes with considerably lower frequencies than those of the ions vibrating in fixed surroundings which would allow the specific heat curve to rise more rapidly at low temperatures. If the group were made large enough and the assumptions as to interatomic forces were correct then one would expect to be able to calculate correctly the specific heat. The hope is that, because of the lack of similarity of neighbors beyond the fourth or fifth nearest neighbors the groups chosen could be small enough for reasonable ease of calculation. If this should prove to be the case we would have a useful tool for calculating other physical properties such as coefficient of expansion. Free energy at any temperature could be computed by the regular methods of statistical mechanics and that network spacing chosen at each temperature such that the free

energy is a minimum. One might even be optimistic enough to foresee that the effect of additions such as any of the usual network modifiers might be so computed.

As an illustration one can take the case of a single SiO_2 group, i.e. any silicon ion and any two of its immediate oxygen neighbors. There will be nine degrees of freedom and there should therefore be nine modes of vibration of this group. The Si will be taken at (0, 0, 0) one oxygen at (s, s, s) and the other at (-s, -s, s). Any three mutually perpendicular axes may be chosen for each ion and one must then investigate what linear combinations of these will give those nine normal co-ordinates which will represent the nine independent modes of vibration.

In order that the three directions chosen for an oxygen ion be independent of one another one should be along the oxygen-silicon line and the other two transverse to it. It is also convenient to choose one of these transverse directions for each oxygen perpendicular to the plane of the SiO_2 group. For the silicon the three directions of motion will be chosen (1) perpendicular to the plane of the SiO_2 group, (2) along the bisector of the O-Si-O angle and, (3) in the SiO_2 plane perpendicular to the bisector. The direction cosines of these directions are given below:

| | |
|-------------------|--|
| First oxygen: | Location (s, s, s) |
| Co-ordinate x_1 | Direction ($\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}$) along Si-O ₁ line |
| Co-ordinate x_2 | Direction ($\frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}}, 0$) perpendicular to SiO ₂ plane |
| Co-ordinate x_3 | Direction ($\frac{1}{\sqrt{6}}, \frac{1}{\sqrt{6}}, -\frac{2}{\sqrt{6}}$) |
| Second oxygen | Location (-s, -s, s) |
| Co-ordinate x_4 | Direction ($-\frac{1}{\sqrt{3}}, -\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}$) along SiO ₂ line |
| Co-ordinate x_5 | Direction ($\frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}}, 0$) perpendicular to SiO ₂ plane |
| Co-ordinate x_6 | Direction ($-\frac{1}{\sqrt{6}}, -\frac{1}{\sqrt{6}}, -\frac{2}{\sqrt{6}}$) |
| Silicon | Location (0, 0, 0) |
| Co-ordinate x_7 | Direction ($\frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}}, 0$) perpendicular to SiO ₂ plane |
| Co-ordinate x_8 | Direction ($\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0$) perpendicular to O-Si-O bisector |
| Co-ordinate x_9 | Direction (0, 0, 1) along O-Si-O bisector |

If co-ordinate x_m is given a value x_m and if the force exerted on the ion whose co-ordinate is x_n along the x_n direction is F_{mr} then the quantity k_{mn} will be defined such that

$$F_{mn} = -k_{mn} x_m \quad (41)$$

From the symmetrical form of equations (38) and (40) it is apparent that

$$k_{m,u} = k_{u,m}$$

The three quantities k_{si} and k_L and k_T will be defined as follows.

If a silicon ion is displaced a distance u while all other ions are held at rest the force on the silicon ion will be

$$k_{si} u$$

If an oxygen ion is displaced a distance u along the oxygen-silicon line the force exerted on it will be (all other ions remaining in positions)

$$k_L u$$

If an oxygen ion is displaced a distance u in a transverse direction the force on it will be (all other ions remaining positive)

$$k_T u$$

For equilibrium it is clear that k_{si} , k_L and k_T are all negative quantities. Their numerical values have already been given in expressions (31), (32) and (33).

Since a number of the k_{mn} 's go to zero it is convenient to evaluate these before writing down the equations of motion in each of the nine co-ordinates. From our choice of co-ordinates it is clear that k_{12} , k_{23} , k_{31} , k_{45} , k_{56} , k_{64} , k_{78} , k_{89} , and k_{97} are all zero. The values of the rest are given below:

$$k_{14} = -\frac{20}{3} \frac{e^2}{r_+^3} - \frac{B}{3r_+^{n+1}} (2n+1)$$

$$k_{15} = 0$$

$$k_{16} = -\frac{4\sqrt{2}}{3} \frac{e^2}{r_+^3} - \frac{B\sqrt{2}}{3r_+^{n+1}} (n-1)$$

$$k_{24} = 0$$

$$k_{25} = -4 \frac{e^2}{r_+^3} - \frac{B}{r_+^{n+1}}$$

$$k_{26} = 0$$

$$k_{34} = -\frac{4\sqrt{2}}{3} \frac{e^2}{r_+^3} - \frac{B\sqrt{2}}{3r_+^{n+1}} (n-1)$$

$$k_{35} = 0$$

$$k_{36} = -\frac{16}{3} \frac{\epsilon^2}{r_i^3} - \frac{B}{3 r_i^{n+1}} (n+2)$$

$$k_{17} = 0$$

$$k_{18} = -\frac{32}{\sqrt{6}} \frac{\epsilon^2}{r_i^3} + \frac{2 A n}{\sqrt{6} r_i^{n+1}}$$

$$k_{19} = -\frac{16}{\sqrt{3}} \frac{\epsilon^2}{r_i^3} + \frac{A n}{\sqrt{3} r_i^{n+1}}$$

$$k_{27} = 8 \frac{\epsilon^2}{r_i^3} - \frac{A}{r_i^{n+1}}$$

$$k_{28} = 0$$

$$k_{29} = 0$$

$$k_{37} = 0$$

$$k_{38} = \frac{8}{\sqrt{3}} \frac{\epsilon^2}{r_i^3} - \frac{A}{\sqrt{3} r_i^{n+1}}$$

$$k_{39} = -\frac{16}{\sqrt{6}} \frac{\epsilon^2}{r_1^3} + \frac{2A}{\sqrt{6} r_1^{n+1}}$$

$$k_{47} = 0$$

$$k_{48} = \frac{32}{\sqrt{6}} \frac{\epsilon^2}{r_1^3} - \frac{2A}{\sqrt{6} r_1^{n+1}}$$

$$k_{49} = -\frac{16}{\sqrt{3}} \frac{\epsilon^2}{r_1^3} + \frac{A}{\sqrt{3} r_1^{n+1}}$$

$$k_{57} = 8 \frac{\epsilon^2}{r_1^3} - \frac{A}{r_1^{n+1}}$$

$$k_{58} = 0$$

$$k_{59} = 0$$

$$k_{67} = 0$$

$$k_{68} = -\frac{8}{\sqrt{3}} \frac{\epsilon^2}{r_1^3} + \frac{A}{\sqrt{3} r_1^{n+1}}$$

$$k_{69} = -\frac{16}{\sqrt{6}} \frac{\epsilon^2}{r_1^3} + \frac{2A}{\sqrt{6} r_1^{n+1}}$$

(43)

The nine equations of motion may then be set up omitting terms for which the k's are zero.

$$k_{11}x_1 + k_{14}x_4 + k_{16}x_6 + k_{18}x_8 + k_{19}x_9 = m_0 \frac{d^2x_1}{dt^2} \quad (44)$$

$$k_{27}x_2 + k_{25}x_5 + k_{27}x_7 = m_0 \frac{d^2x_2}{dt^2} \quad (45)$$

$$k_{37}x_3 + k_{34}x_4 + k_{36}x_6 + k_{38}x_8 + k_{39}x_9 = m_0 \frac{d^2x_3}{dt^2} \quad (46)$$

$$k_{10}x_1 + k_{34}x_3 + k_{14}x_4 + k_{43}x_8 + k_{49}x_9 = m_0 \frac{d^2x_4}{dt^2} \quad (47)$$

$$k_{25}x_2 + k_{27}x_5 + k_{27}x_7 = m_0 \frac{d^2x_5}{dt^2} \quad (48)$$

$$k_{16}x_1 + k_{36}x_3 + k_{27}x_6 + k_{68}x_8 + k_{69}x_9 = m_0 \frac{d^2x_6}{dt^2} \quad (49)$$

$$k_{27}x_2 + k_{25}x_5 + k_{57}x_7 = m_{5c} \frac{d^2x_7}{dt^2} \quad (50)$$

$$k_{18}x_1 + k_{38}x_3 + k_{48}x_4 + k_{68}x_6 + k_{58}x_8 = m_{5c} \frac{d^2x_8}{dt^2} \quad (51)$$

$$k_{19}x_1 + k_{39}x_3 + k_{49}x_4 + k_{69}x_6 + k_{59}x_9 = m_{5c} \frac{d^2x_9}{dt^2} \quad (52)$$

Co-ordinates x_2 , x_5 and x_7 are independent of all the other co-ordinates. Further, because $k_{27} = k_{57}$ equations (45) and (48) can be combined to give

$$(k_{27} - k_{25})(x_2 - x_5) = m_0 \frac{d^2}{dt^2} (x_2 - x_5) \quad (53)$$

which gives immediately one of the independent modes of vibration and corresponds to both oxygen ions vibrating perpendicular to the SiO_2 plane so that one is always as far on one side as the other is on the other side. Such a motion can continue without exciting any of the other co-ordinates into motion.

Similarly equations (45), (48) and (50) may be combined by multiplying both sides of (50) by some number λ and adding (using the fact that $k_{27} = k_{57}$)

$$(\chi_2 + \chi_5)(k_7 + k_{25} + \lambda k_{17}) + \chi_7(2k_{17} + \lambda k_2) = m_o \frac{d^2}{dt^2}(\chi_2 + \chi_5) + \lambda m_{\text{Si}} \frac{d^2 \chi_7}{dt^2} \quad (54)$$

If λ is so chosen that

$$\frac{k_7 + k_{25} + \lambda k_{17}}{2k_{17} + \lambda k_2} = \frac{m_o}{\lambda m_{\text{Si}}} \quad (55)$$

then equation (54) will reduce to a simple harmonic equation for the co-ordinates

$$\chi_2 + \chi_5 + \lambda \frac{m_{\text{Si}}}{m_o} \chi_7 \quad (56)$$

Actually equation (55) yields two such values of λ giving all of the three (counting equation (53)) independent modes

of the co-ordinates x_2 , x_5 and x_7 .

To obtain the other six modes of vibration it should be noted from equations (43) that

$$k_{16} = k_{34} \quad (57)$$

$$k_{18} = -k_{48} \quad (58)$$

$$k_{19} = k_{49} \quad (59)$$

$$k_{38} = -k_{68} \quad (60)$$

$$k_{39} = k_{69} \quad (61)$$

Using these relations equations (44), (46), (47), (49) and (52) may be combined to give

$$k_2(x_1 + x_4) + k_{14}(x_1 + x_4) + k_{16}(x_3 + x_6) + 2k_{19}x_9 = m_0 \frac{d^2}{dt^2} (x_1 + x_4) \quad (62)$$

$$k_{16}(x_1 + x_4) + k_7(x_3 + x_6) + k_{36}(x_3 + x_6) + 2k_{39}x_9 = m_0 \frac{d^2}{dt^2} (x_3 + x_6) \quad (63)$$

$$k_{14}(x_1 + x_4) + k_{36}(x_3 + x_6) + k_{56}x_9 = m_{56} \frac{d^2 x_9}{dt^2} \quad (64)$$

of the co-ordinates x_2 , x_5 and x_7 .

To obtain the other six modes of vibration it should be noted from equations (43) that

$$k_{16} = k_{34} \quad (57)$$

$$k_{18} = -k_{48} \quad (58)$$

$$k_{19} = k_{49} \quad (59)$$

$$k_{38} = -k_{68} \quad (60)$$

$$k_{39} = k_{69} \quad (61)$$

Using these relations equations (44), (46), (47), (49) and (52) may be combined to give

$$k_{12}(x_1 + x_4) + k_{14}(x_1 + x_4) + k_{16}(x_3 + x_6) + 2k_{19}x_9 = m_0 \frac{d^2}{dt^2} (x_1 + x_4) \quad (62)$$

$$k_{16}(x_1 + x_4) + k_{17}(x_3 + x_6) + k_{36}(x_3 + x_6) + 2k_{39}x_9 = m_0 \frac{d^2}{dt^2} (x_3 + x_6) \quad (63)$$

$$k_{14}(x_1 + x_4) + k_{39}(x_3 + x_6) + k_{51}x_9 = m_0 \frac{d^2 x_9}{dt^2} \quad (64)$$

If (63) is multiplied by L_1 and (64) by β_1 , there is obtained

$$\begin{aligned} & (k_L + k_{14} + L_1 k_{16} + \beta_1 k_{19})(x_1 + x_4) + (k_{16} + L_1 k_T + L_1 k_{36} + \beta_1 k_{39})(x_5 + x_6) \\ & + (2k_{19} + 2L_1 k_{39} + \beta_1 k_{51})x_9 = m_0 \frac{d^2}{dt^2} \{ (x_1 + x_4) + L_1 (x_5 + x_6) \} + \beta_1 m_{s1} \frac{d^2 x_9}{dt^2} \end{aligned} \quad (65)$$

This transforms to a simple harmonic equation in the variable $x_1 + x_4 + L_1(x_5 + x_6) + \beta_1 x_9$ where $\rho = \frac{m_{s1}}{m_0}$ if the following two relations hold

$$\frac{k_L + k_{14} + L_1 k_{16} + \beta_1 k_{19}}{k_{16} + L_1 k_T + L_1 k_{36} + \beta_1 k_{39}} = \frac{1}{L_1} \quad (66)$$

and

$$\frac{k_L + k_{14} + L_1 k_{16} + \beta_1 k_{19}}{2k_{19} + 2L_1 k_{39} + \beta_1 k_{51}} = \frac{1}{\rho \beta_1} \quad (67)$$

These may be rearranged to yield

$$\beta_1 = \frac{k_{16} + L_1(k_T + k_{36} - k_L - k_{14}) - L_1^2 k_{16}}{L_1 k_{19} - k_{39}} \quad (68)$$

$$\chi_1 = \frac{2k_{14} + 3(k_{51} - \rho k_{12} - \rho k_{14}) - \beta_1 \rho k_{19}}{\beta_1 \rho k_{16} - 2k_{39}} \quad (69)$$

which can be solved graphically for χ_1 and β_1 . There are three pairs of values for χ_1 and β_1 yielding three more of the nine modes of vibration. The final three may be found by combining (44), (46), (47), (49) and (51) to yield

$$-k_{12}(\chi_1 - \chi_4) - k_{14}(\chi_1 - \chi_4) - k_{16}(\chi_3 - \chi_6) + 2k_{18}\chi_8 = m_0 \frac{d^2}{dt^2} (\chi_1 - \chi_4) \quad (70)$$

$$-k_{16}(\chi_1 - \chi_4) + k_{17}(\chi_3 - \chi_6) - k_{36}(\chi_3 - \chi_6) + 2k_{38}\chi_8 = m_0 \frac{d^2}{dt^2} (\chi_3 - \chi_6) \quad (71)$$

$$k_{18}(\chi_1 - \chi_4) + k_{38}(\chi_3 - \chi_6) + k_{51}\chi_8 = m_{51} \frac{d^2 \chi_8}{dt^2} \quad (72)$$

Again multiplying (71) by χ_2 and (72) by β_2 and combining there is obtained an equation which will be a simple harmonic equation in the variable

$$(\chi_1 - \chi_4) + \chi_1 (\chi_3 - \chi_6) + \beta_2 \rho \chi_8 \quad \text{if } \chi_2 \text{ and } \beta_2$$

are connected by relations similar to (68) and (69) and which actually are

$$\beta_2 = \frac{k_{16}(\chi_2^2 - 1) + \chi_2(k_{17} - k_{36} - k_{12} - k_{14})}{\chi_2 k_{18} - k_{38}}$$

$$\chi_2 = \frac{k_{18}(\beta_2^2 - 2) + \beta_2(\rho k_{12} - \rho k_{14} - k_{51})}{2k_{38} + \beta_1 \rho k_{16}}$$

This again may be solved graphically yielding three pairs of values for α_2 and β_2 and giving the final three modes of vibrations.

It remains to insert the numerical values for the k's and determine whether the move toward this larger group is an improvement over use of the single vibrations of the separate ions. When this is done there are obtained nine frequencies and nine characteristic temperatures for the SiO_2 group. These temperatures are listed below in order of increasing magnitude

795°K
962
985
1020
1332
1518
1601
2376
2477

Of these the first four correspond to modes where transverse oxygen vibrations are dominant. The next three

arise from modes where a silicon vibration is dominant and finally in the last two a longitudinal oxygen vibration is dominant. The larger group has introduced some lower characteristic temperatures and gives a slightly better but still not good agreement with the experimental values. Presumably now if the assumptions as to structure and forces between ions were correct and if the various approximations used along the way were justified, then by choosing a large enough neutral group of ions and working out all the proper modes of vibrations of this group a specific heat curve could be computed which would fit the experimental data. Unfortunately, to work out mathematically the proper modes of vibration for any group larger than that treated above requires a prohibitively long computation.

However, it is possible to set up an electrical analogue in which the movements of charges are determined by exactly the same equations of motion as would govern the movements of ions. As an illustration, the circuit of fig. 2A represents the circuit for an ion vibrating in one direction independent of the motions of its neighbors. The charge on the condenser corresponds to the displacement of the ion, the inductance L corresponds to the mass of the ion and the reciprocal of the capacity C corresponds to the restoring force per unit displacement.

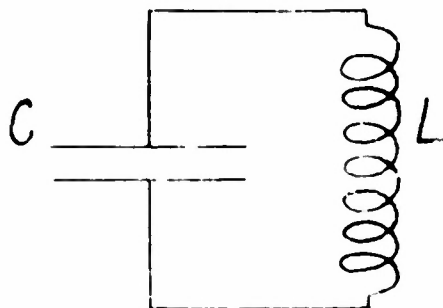


FIG 2 A

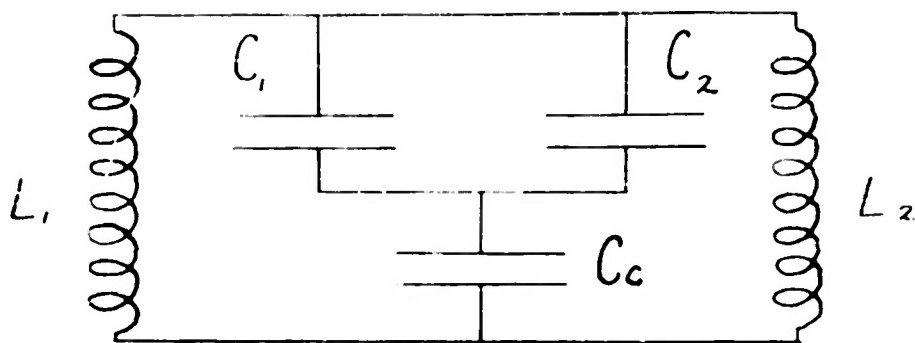


FIG. 2 B

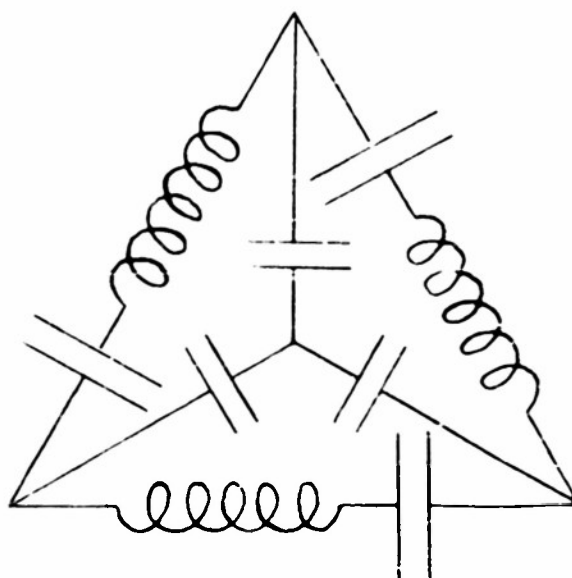


FIG 2 c.

By virtue of equation (42) this analogue may be extended to two ions where the movement of one causes a force on the other, and vice versa. Here L_1 represents the mass of ion (1) and L_2 the mass of ion (2). The quantity $\frac{1}{C_1} + \frac{1}{C_c}$ represents the restoring force on ion (1) because of all its neighbors at rest and $\frac{1}{C_2} + \frac{1}{C_c}$ represents the corresponding quantity for ion (2). $\frac{1}{C_c}$ represents the force on ion (1) for a unit displacement of ion (2) or (by equation (42)) the force on ion (2) caused by a unit displacement of ion (1).

Fig. 2c represents one of the possible ways in which three degrees of freedom could be coupled together. It is planned to use such a system in the investigation of the proper modes of vibration of larger neutral groups. A large frequency range can be covered with a vacuum tube oscillator and the resonant frequencies can easily be picked up with a vacuum tube voltmeter or oscillograph.

Future Work

The methods developed here give a means of quantitatively checking the experimental values of specific heat with any chosen field of force between the constituent atoms or ions. The first agreement is not good and the most obvious places to try to improve the assumptions made are as listed below:

(1) Choice of pure ionic model. Possibly a mixture of this model and a model showing also potential energies between nearest neighbors of a form like a Morse function might give better results. Constants would be chosen so as to give agreement between the calculated and experimental heats of formation.

(2) Inclusion of more ions in the groups considered to vibrate independently. This has already been discussed.

(3) A good detailed geometrical investigation of the probable deviations from the regular cristobalite structure. It should be possible to find a limited number of ways of introducing the irregularities which differentiate the vitreous state from the crystalline state. From the results of the paper on Compressibility of Vitreous Silica by Smyth, Londere and Lorey it appears that because of such irregularities some but not all of the Si-O-Si lines are actually bent. This would lower the frequency of the transverse vibrations and help to give a better fit with the experimental specific heat curve at lower temperatures.

If by one or more of these methods it is found possible to get a reasonably good agreement between calculated and experimental specific heat values using a reasonably limited number of independent modes of vibration it should be possible

to set up the partition function for the system and calculate the free energy at any temperature and any Si-O spacing. Minimizing the free energy at each temperature would allow calculation of the thermal expansion. In view of the fact that at moderately low temperatures only the transverse oxygen frequency plays any important part and since it is easy to show from equation (22) that on the basis of the model considered this frequency decreases rather than increases with decreasing volume it seems very probable that this alone will be sufficient to explain the negative and low expansion of vitreous silica at low temperatures. Extension of this work to glasses containing a second oxide might not be out of the question.

Conclusions

The results show that a calculation of the frequencies of vibration of silicon and oxygen ions separately on a pure ionic model is not sufficient to get a good agreement between calculated and experimental specific heat values for vitreous silica. They also show several ways in which this very naive picture may be modified to give better agreement.

The fact that the transverse vibration, which is the only important one at low temperatures, decreases with decreasing volume suggests that this may be the cause of the negative expansion of vitreous silica at low temperature. A more detailed investigation of this is planned in a later paper.

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